

Growth mechanisms in chemical vapour deposited carbon nanotubes

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Received 27 September 2002, in final form 6 February 2003

Published 17 April 2003

Online at stacks.iop.org/Nano/14/655

Abstract

We present a model for the process of the growth of carbon nanotubes (CNTs) obtained by chemical vapour deposition in the presence of transition metal nanoparticles (Me-NPs) which act as a catalyst. We have deduced that the growth of a CNT occurs in the presence of two forces: (i) a viscous force, due to the surrounding hot gas, which opposes and slows down the growth of the CNT, and (ii) an extrusive force that causes the growth and that in the steady-state stage of the growth is completely balanced by the viscous force. We believe that it is the great decrease in free energy in the assembling reaction that occurs at the interface of the Me-NP catalyst that causes the extrusive force for the growth of a CNT. Moreover, the process of chemisorption of a C₂ fragment, through the interaction of the C₂- π system with the 3d metal orbitals, has been considered as well as the coordination action of the Fe, Ni and Co metal surfaces. The structural properties of the Fe, Co and Ni surfaces show that the (1, -1, 0) planes of Fe and the (1, 1, 1) planes of Co and Ni exhibit the symmetry and distances required to overlap with the lattice of a graphene sheet. This gives us information about the coordination mechanism responsible for assembling the CNTs. In fact, we show that it is possible to cleave an Me-NP in such a way as to match the correct symmetry and dimension of the armchair structure of a single-walled nanotube. The mechanism of C₂ addition at the edge of the growing CNT has also been considered in relation to the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) symmetry. We demonstrate that the action of d orbitals of the metal atoms forming the Me-NP makes possible the thermally forbidden reaction, which involves the C₂- π system.

1. Introduction

Carbon nanotubes (CNTs) have stimulated a great deal of interest in the microelectronics industry because of their unique conducting properties enabling the manufacture of devices such as field effect transistors (FETs) [1–3], field emission displays (FEDs) [4] or single electron transistors (SETs) [5, 6]. This makes them one of the most promising materials in the field of molecular electronics.

CNTs are hollow cylindrical shaped carbon molecules that because of their nanometric diameter can be thought of as

molecular nanowires. In particular, the properties of a single-walled nanotube (SWNT) are determined by the graphene structure in which the carbon atoms are arranged to form a cylinder. This structure can be described in terms of a chiral vector C which considers the arrangement of the graphite hexagons with respect to the CNT axis. The chiral vector C is completely defined by specifying a pair of two integer numbers (n, m) identifying the two components of C with respect to the lattice parameters of the graphene sheet. In particular, SWNTs can be classified as armchair (n, n) nanotubes if $n = m$, as zig-zag $(n, 0)$ nanotubes if $m = 0$ and as chiral nanotubes for the other cases.

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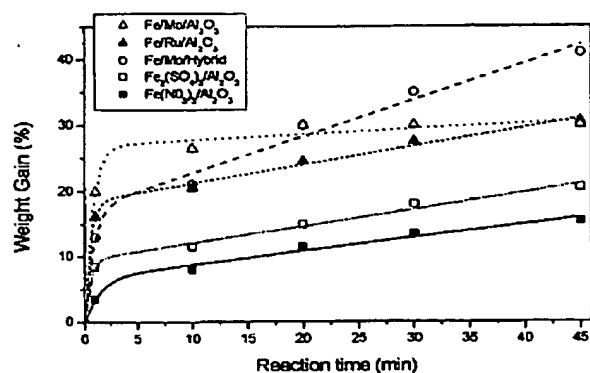
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Figure 1. Weight gain versus reaction time (from [1]). Almost half of the growth occurs during the first minute independently on the Fe catalyst used, while in the following 44 min the growth occurs at a slower or stationary rate.

CNTs have been obtained using several techniques such as arc discharge [7], laser ablation [8] and chemical vapour deposition (CVD) [9–11]. In the first two cases, CNTs are obtained after the condensation of a hot carbon gas, while in the latter case the growth of a CNT is determined by the presence of a catalyst, usually a transition metal such as Fe, Co or Ni, which causes the catalytic dehydrogenation of hydrocarbons and consequently the formation of a CNT. In particular, the use of the CVD technique in the growth of CNTs is of great interest since it fits in with the integration process used in the microelectronic industry.

These metals (Fe, Co or Ni), deposited for example on a nano-patterned support such as alumina or a nanoporous medium (porous silicon), undergo a calcination process that forms metal nanoparticles (Me-NPs). After that, the Me-NP catalyst is involved in a pyrolysis that, starting from a hydrocarbon (CH_4 , C_2H_2 , C_6H_6), determines the growth of CNTs. Carbon residues are formed as a consequence of the catalytic dehydrogenation of the hydrocarbon molecules on the Me-NP surface.

The growth mechanisms are essentially divided into base growth or tip growth, depending on whether the Me-NP remains anchored at the support or not, respectively. This clearly depends on the strength of the interaction between the nanoparticle and the support.

In this paper we present a model which gives clues to the understanding of the growth mechanism of CNTs. By focusing on the case of SWNTs, we will be able to consider the action of transition Me-NPs. And in particular, by considering their structural properties for the cases of Fe, Ni and Co we will show a correlation between armchair nanotubes and Me-NP structure.

2. Extrusive-diffusive model

A macroscopic and reasonable growth mechanism for CNTs can be deduced by following the development of the relative weight gain of the CNTs (proportional to the average length of the CNTs) with the reaction time as reported by Cassell *et al* [9] for the case of SWNTs and reproduced in figure 1. From

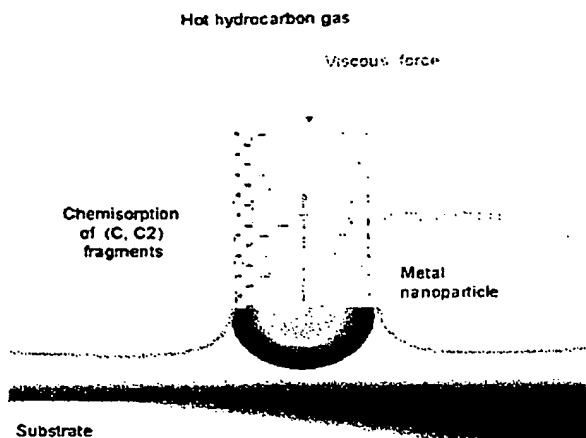


Figure 2. Sketch of the growth process. The viscous force should be applied to the centre of mass of the system.

the graph, we can observe that almost half of the growth occurs during the first minute, independently of the Fe catalyst used, while in the following 44 min the growth proceeds at a slower or stationary rate.

Bearing this in mind, and considering that the continuous feedstock of carbon atoms comes from a hot and dense gas surrounding the growing CNT (necessary in order to gather many carbon atoms on the Me-NP), we can conclude that the CNT growth process occurs in a diffusive regime where surrounding hot gases provide a viscous force that slows down CNT growth. Moreover, in our empirical model all the processes that oppose the growth are also included within the friction force. However, one friction force alone cannot explain the growth mechanism. We need to invoke the presence of another force in order to form a CNT from an Me-NP.

A simple model of the growth process is schematically depicted in figure 2, by considering that the average length l of a tube is directly connected with the average growing speed (i.e. $v = dl/dt$), that the friction force can be modelled proportionally to the growing speed v (i.e. $F = -bv$ where b is a friction coefficient) and that the extruding force F_{ex} is a constant force. Therefore, according to the second law of dynamics:

$$m \frac{dv}{dt} = F_{ex} - bv \quad (1)$$

where, in the case of growth from the base, the mass m is the growing mass of a CNT. This equation can describe reasonably well the general behaviour of CNT growth in the stationary stage, where the stationary speed is $v_{st} = F_{ex}/b$. On the other hand, the description of the growth fails for the initial stage because of the discrete nature of the addition of atoms that cannot be described well by a continuous model. For this reason, near the steady state the growing mass of the CNT can be approximated by $m = \lambda vt + m_0$, where λ is the linear density of the growing nanotube. Clearly, when the steady state is reached, the speed v is quite slow. Therefore we can approximate the mass of the CNT with a fictitious constant

Table 1. Fitting parameters from data of [1] (fitting equation $wg = At + (B - A)C[1 - \exp(-t/C)]$).

	$A \propto v_{st}(\text{min}^{-1})$	$B \propto v_0(\text{min}^{-1})$	$m/b(\text{min})$
$\text{Fe}(\text{NO}_3)_3/\text{Al}_2\text{O}_3$	0.21	4.7	1.5
$\text{Fe}_2(\text{SO}_4)_3/\text{Al}_2\text{O}_3$	0.26	19.3	0.5
$\text{Fe}/\text{Ru}/\text{Al}_2\text{O}_3$	0.56	22.7	0.8
$\text{Fe}/\text{Mo}/\text{hybrid}$	0.28	37.8	0.5
$\text{Fe}/\text{Mo}/\text{Al}_2\text{O}_3$	0.08	36.4	0.74

mass m . This allows us to integrate the preceding equation exactly, and by introducing the initial condition that the tube starts its growth with a certain speed v_0 we obtain that the average length and hence the weight gain (wg) must follow the law:

$$wg \propto t = v_{st}t + (v_0 - v_{st})m/b[1 - \exp(-b/m)t]. \quad (2)$$

A fit of the experimental data has been tested in figure 1, applying this law with three parameters. Two of them are proportional to v_{st} and v_0 due to the wg, with the same constant of proportionality, while the third parameter is m/b ; the values of these parameters are given in table 1.

We observe that as $v_0 \gg v_{st}$ for all cases the growth slows down considerably towards the steady state. In this regime the model states that the viscous and the extruding forces are completely balanced. This empirical model allows us to follow the growth without any distinction between a first stage and a steady stage in nanotube formation and invokes the presence of a unique cause, i.e. the extruding force, as being responsible for the growth.

What, therefore, is the origin of the extruding force that drives and pushes off the CNTs from the surface? In a growing nanotube a continuous reaction occurs at the interface of the Me-NP. Because of its catalytic action the Me-NP is able to assemble the dehydrogenated carbon fragments in a well-formed CNT. CNTs are stable molecules whose synthesis gives rise to a large and negative variation of the free energy ΔG . Indeed, we have calculated the variation of the free energy ΔG in the reaction in which a dimer is added to a molecule as shown in figure 3, similar to the reaction that should occur in the growth of a CNT.

We estimate a variation $\Delta G = -218 \text{ kcal mol}^{-1}$ ($\sim 10 \text{ eV/atom}$) at 1000 K. This huge free energy drop will be lost if CNTs are formed from a hot carbon gas (arc discharge, laser ablation), but can be used in the case of CNTs formed by CVD in order to do the mechanical work which is able to extrude the CNT. In fact ΔG provides an estimation of the maximal mechanical work that can be performed by the system. The Me-NP therefore favours the chemical assembly of carbon fragments but at the same time directs their growth by determining the energy release which occurs in a well-defined direction. Hence, the extruding force connects with the $-\Delta G$ per unit length of the tube. Our simple model states the importance of the interaction at the interface between the carbon fragments and the Me-NP surface.

3. Structural correlation and molecular mechanisms

Growth models of CNTs formed by arc discharge consider that a CNT grows by addition of C_2 (i.e. dimers) for the case

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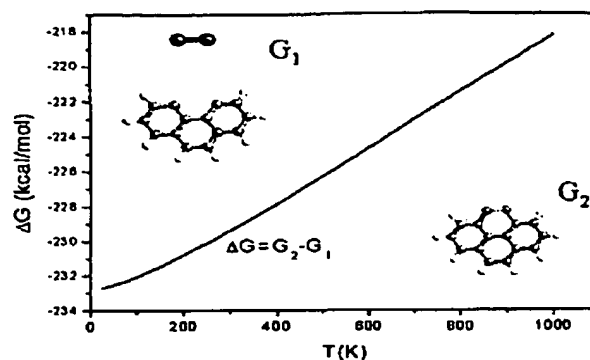


Figure 3. Free energy variation for addition of C_2 at the edge of the structure as a function of temperature.

of armchair CNTs, by the addition of C_3 (i.e. trimers) for the case of zig-zag CNTs, and that growth occurs at the open lip of the tube [12]. Similarly, in the case of SWNTs formed by laser ablation a spectroscopic investigation of the molecular species formed in the plume gives evidence for the existence of excited C_2 dimers [13].

The growth mechanism of CNTs obtained from catalytic nanoparticles take into account the diffusion [10,14] of carbon atoms from the surface of the support into the Me-NP and the consequent extrusion of the walls (for multiwalled nanotubes (MWNTs)) of the formed CNT, with the coordinating action of transition metals [15–18] and with a direct correlation of the tube diameter with that of the Me-NP [19]. Nevertheless, in the case of SWNTs obtained by catalytic pyrolysis of hydrocarbons, diffusion inside the Me-NP is not an essential process, whereas the interaction of carbon atoms or carbon fragments with the Me-NP surface plays a prominent role in the assembly of C atoms in an assigned CNT. In fact, hydrocarbons get rid of their hydrogens, eventually breaking some of their C bonds, and assemble on the Me-NP in order to form a CNT. Therefore, the chemisorption process underlies the catalytic action of Me-NPs. Since SWNTs have been obtained by 3d transition Me-NPs such as Fe, Co and Ni and since light carbon fragments such as C_2 are involved in CNT formation, we will consider that a transition metal can interact with a C_2 fragment.

Chemisorption of carbon fragments, such as a C_2 , on a transition metal surface is favoured due to the presence of π electrons that have the right symmetry to overlap with the 3d electrons. In fact, by considering the molecular orbitals of a C_2 molecule we may observe how a d_{xz}^2 or $d_{x^2-y^2}$ (symmetry e_g) orbital overlaps with a π_{2pz} and π_{2py} orbital respectively while the antibonding π_{2pz}^* overlaps with a d_{xz} (as also the π_{2py}^* overlaps with a filled d_{xy} orbital) (t_{2g} symmetry), in order to form coordinate bonds, as shown in figure 4.

Consequently, a C_2 fragment has two possible positions on the surface of a transition metal, i.e. on the top of the 3d metal atom or between two of them. Therefore, we can explain the coordination mechanism responsible for the assembly of CNTs. In fact, in order to have a cooperative effect in the chemisorption mechanism, the metal atoms on a surface must be in the right position in order to reproduce the lattice structure of a graphene layer, as shown in figure 5(a).

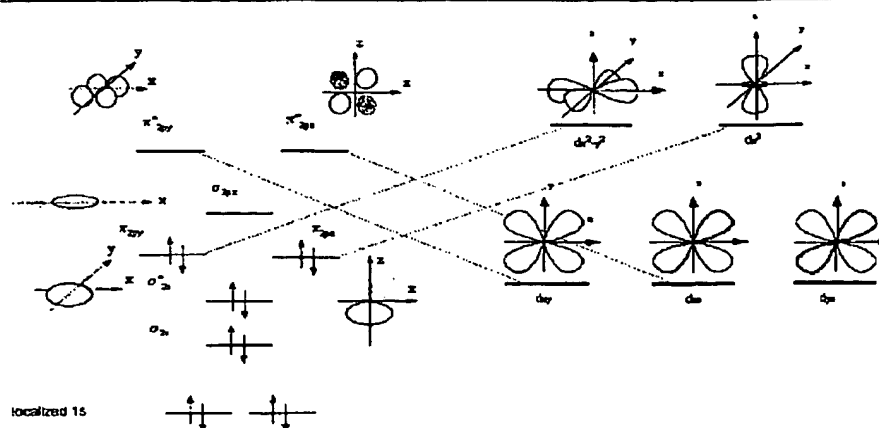


Figure 4. Levels diagram for a C_2 molecule and correlations with d orbitals of a metal atom. In order to have coordinate bonds the d_{xy} or d_{xz} must be filled, as similarly the $d_{x^2-y^2}$ or d_{z^2} must be unfilled. It is worth observing that the energy spacing between the HOMO (π_{2py} , π_{2pz}) and the LUMO (σ_{2pz}) of C_2 is 0.26 eV (local density approximation calculation). As a consequence, in SWNTs obtained by laser ablation the LUMO of C_2 is quite populated.

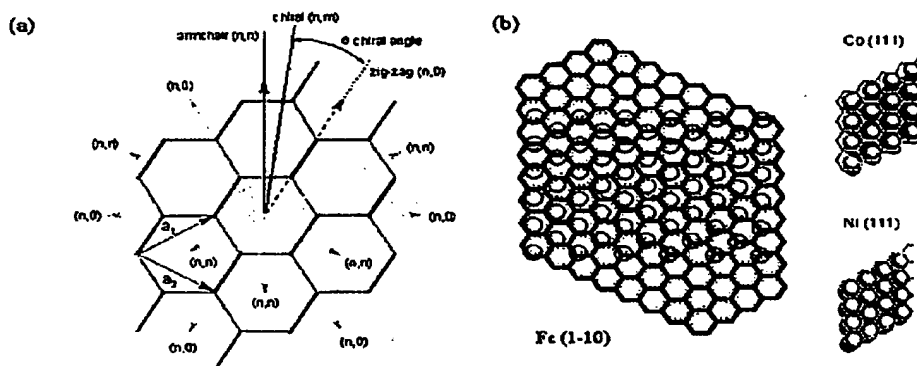


Figure 5. (a) Coordination of chemisorbed C_2 fragments on a metal plane reproducing the lattice structure of a graphene sheet. The thick black lines represent the π bonds of the C_2 fragments. (b) Matching between a Fe (1, -1, 0), a Ni (1, 1, 1) and a Co (1, 1, 1) plane with a graphene sheet. Fe (bcc) lattice constant is $a = 2.86$ Å, the least distance between two Fe atoms on a (1, -1, 0) plane is $d = 2.48$ Å. For Co (1, 1, 1), $a = 3.54$ Å, $d = 2.50$ Å. For Ni (1, 1, 1), $a = 3.52$ Å, $d = 2.49$ Å. The lattice parameter $a_1 = a_2$ for a graphene plane amounts to $a_1 = 2.45$ Å.

A study of Fe, Co and Ni surfaces has shown that the (1, -1, 0) plane of Fe (bcc lattice) and the (1, 1, 1) planes of Co and Ni (fcc lattice) have the appropriate symmetry and distances to overlap with the lattice of a graphene sheet (figure 5(b)). This structural correlation suggests that if the same pattern of metal atoms could be transferred on an opportunely shaped Me-NP, where a well defined direction of growth exists, the growth of SWNTs of well-defined chirality would be possible.

Because of this correspondence between the Fe, Co and Ni surfaces and the graphene layer, we have investigated the possibility that by cleaving an Fe crystal (and also a Co and Ni crystal) it is possible to shape an Me-NP in such a way that it matches the dimensions and symmetry of a CNT structure. The result of such an exercise is shown in figure 6 for the case of (10, 10) and (5, 5) armchair nanotubes for Fe and Ni (similar results are obtained in the case of Co Me-NPs, not shown here). This structural correspondence suggests hence that a strong correlation exists between the surface of Me-NPs

and the SWNT structure. Clearly we suppose that the growth we are considering occurs at 'low temperature' so that the Me-NPs are not in the liquid phase.

Addition of C_2 at the edge of the growing nanotubes is a reasonable mechanism of growth in the case of an armchair nanotube, because of the C_6 ring closure [20]. This mechanism suggests that a concerted reaction can underlie the growth of an SWNT. For this reason the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) symmetry (figure 7(a)) at the edge of the growing nanotube has been compared with the C_2 HOMO-LUMO orbitals (figure 7(b)).

In the concerted addition of the C_2 to the edge of an armchair nanotube, during the reaction event, two elements of symmetry are kept: the plane perpendicular to the armchair structure containing the axis of the tube and the plane perpendicular to the axis containing the atoms at the edge. The HOMO-LUMO or frontier molecular orbitals (figure 7(a)) of

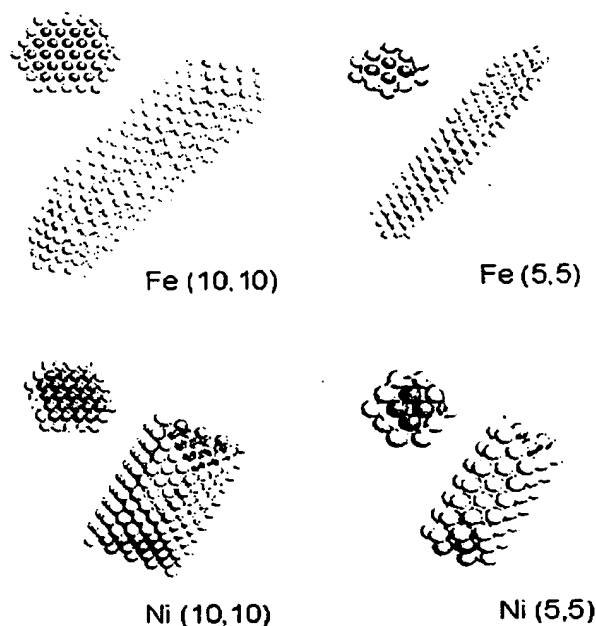


Figure 6. Me-NPs (nanorods) cleaved from the Fe (bcc) and Ni (fcc) metal structures respectively, and matching the symmetry of armchair (10,10) and (5,5) nanotubes (in yellow). The metal surface atoms have been highlighted for clarity. The diameters of Me-NPs so obtained match with those of (10,10) nanotubes ($d = 1.4$ nm) and of (5,5) nanotubes ($d = 0.7$ nm), respectively.

an 'open' nanotube are determined by the linear combination of the p electrons (p_y orbitals according to the reference frame designated in figure 7(b)) of those carbon atoms that are at the edge. The symmetry properties of the two frontier molecular orbitals determine the reactivity of a CNT. In particular, we observe that the HOMO structure (figure 7(a)) is symmetrical (S) with respect to the plane perpendicular to the armchair structure, whereas the LUMO structure is antisymmetrical (A).

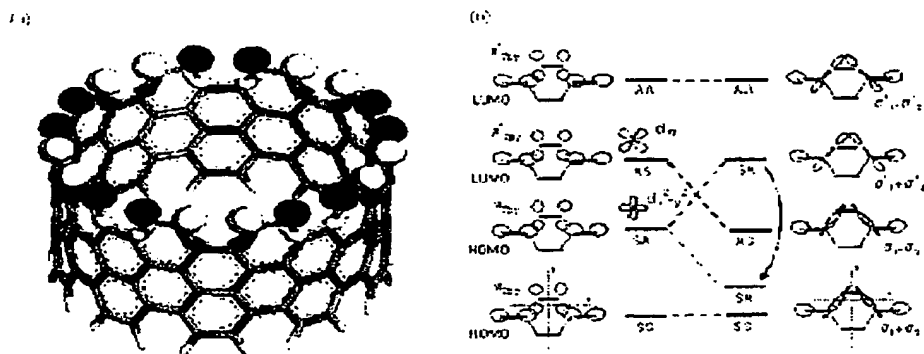


Figure 7. (a) HOMO of a (10,10) nanotube (calculated with DMol³) [21]. The lobes, determined by the combination of p electrons at the edge of the tube, are symmetrical (S) with respect to the armchair structure. The LUMO (not shown here) is similar to the HOMO but antisymmetrical (A) with respect to the same plane. (b) Schematic correlation diagram of the πC_2 -CNT system for the addition of C_2 to the armchair edge structure of the CNT involving the HOMO-LUMO structure of a (10,10) nanotube and the bonding and antibonding orbitals formed by the C_2 - π system, where the action of 3d transition metal orbitals is also considered.

In order to understand how the edge structure of a nanotube can interact with a C_2 fragment in a concerted reaction we have to consider how the HOMO-LUMO structure of the C_2 light fragments can overlap with the HOMO-LUMO of the CNT. By comparing the molecular orbitals of C_2 (reported in figure 4) we may observe that the σ_{2p_x} LUMO of a C_2 is symmetrical (S) with respect to the planes described above and can be overlapped with the HOMO of the CNT. However, the LUMO of the CNT does not overlap with the HOMO of a C_2 formed by two perpendicular π orbitals (figure 4). In order to have a favourable overlap of the C_2 - π system with the HOMO-LUMO structure of a CNT, we need to involve an excited level. Nevertheless, in the case of CNTs obtained by laser ablation the C_2 fragments are excited [13], meaning that the π system must be considered in the concerted reaction.

The role of the π orbitals of the C_2 in the πC_2 -CNT interaction can be summarized in a schematic correlation diagram shown in figure 7(b). In this diagram the states that are involved before the addition of C_2 (left) and after the reactive event (right) are reported and classified as symmetric (S) and antisymmetric (A) with respect to the two planes of symmetry described above. Moreover in the reaction, which considers that the π bonds of a C_2 fragment break and transform into σ bonds, those states of the same symmetry are correlated. All the states involved in the addition of C_2 are classified by means of the two indices S and A. The first index determines the symmetry of the orbitals with respect to the plane containing the tube axis and perpendicular to the armchair structure. The second index fixes the symmetry with respect to the plane perpendicular to the tube axis. The correlated levels in the absence of a catalyst are marked in bold. In this case the upper bonding level of the reactants (C_2 + edge of a CNT), which is an SA bonding state (left), evolves into the lowest SA antibonding state of the product (right), determining a thermally forbidden reaction. We can conclude that the involvement of the π system is not thermally allowed and a higher level (marked with AS in the diagram) is required in order to obtain the addition of C_2 .

On the other hand we have seen that the presence of a transition metal in the form of Me-NP acts as a catalyst and can help the chemisorption process and hence the coordination mechanism, because of the overlap of 3d orbitals with the C₂ fragments (figure 4). The same coordination of 3d orbitals can explain how the atoms of an Me-NP act and make possible thermally forbidden concerted reactions. In fact, as also shown in figure 7(b), an unfilled d_{x²-y²} orbital can overlap with the SA orbital system and lower the energy of this level (the arrow in figure 7(b)) describes this effect and leads to the new level) whereas in the same way a filled d_{xy} orbital can overlap with the AS orbital system. In this way a transition from a bonding level system of the reactants towards a bonding level systems of the products with a lower energy can occur and the reaction becomes thermally allowed.

4. Conclusions

In conclusion we have deduced that the CVD growth of CNTs is determined by an extrusive force opposing a viscous force. This extrusive force originates from the free energy release that occurs at the surface of an Me-NP when the C fragments assemble to form a CNT. This indicates the importance of the interaction of C fragments with the Me-NP surface.

Chemisorption of C₂ molecules due to interaction with the d orbitals of transition metals, along with a structural matching of Fe, Co and Ni planes with a graphene sheet, suggest a mechanism for C₂ formation. In particular, Me-NPs match the symmetry of SWNTs in the case of armchair nanotubes. A concerted reaction determines the assembly of the tubes, which is aided by the coordination action of the Me-NP catalyst.

Acknowledgment

The authors acknowledge Accelrys Inc. for the use of the software DMol³.

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